

# First Law of Thermodynamics

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Be prepared for a journey, but don't expect a destination.

- Craig F. Bohren, Atmospheric Thermodynamics.

## Introduction

A lot of things is difficult to understand in thermodynamics. Good example is heat capacity, defined as added heat over temperature rise. Nothing wrong with it until you went to a phase transition where temperature is constant and heat capacity fly to infinity. The first law of thermodynamics is among those things, which is not obvious on the first look.

## The First Law

All books on thermodynamics mentioned extreme importance of the first law. The equivalent to the first law is that perpetual motion machines of the first kind are impossible.

In other words the first law of thermodynamics is the law of energy conservation.

The first law states that the total energy of an isolated system is constant, energy can be transformed from one form to another, but can be neither created nor destroyed.

Such statement sounds about right, isn't it? No concern about it, the questions began only after formulation:

$$\Delta U = Q - W \quad (1)$$

where  $\Delta U$  denotes change in internal energy of a closed system,  $Q$  denotes the energy supplied to the system as heat, and  $W$  denotes the amount of work done by the system.

The strangeness of the formula are the following: it is absolutely not clear what the heat is. The heat could not be measured directly. Sometimes the amount of heat is in proportion to the temperature, sometimes not (in case of phase transition for example). Internal energy also could not be measured. Any non-conserved amount of energy could be easily referred to internal energy. The only physical value here is amount of work, which could be measured by lifting of weight.

The discussion about heat is the subject for another article and will not be touch here.

Simple experiment described below questioned the first law of thermodynamics.

## Experiment

The experiment is a simple burning of the hydrogen in the atmosphere of oxygen. Experiment will be conducted inside a thermostat, which is a very good approximation of an isolated system for the short time terms. Let us remember the chemical formula of such a reaction:



Looking back at the first law (1) – there is no heat transfer with the surroundings because of the thermostat ( $Q = 0$ ) and no work performed on the surroundings ( $W = 0$ ) and hence it should be no change in internal energy of the system. Let us check.

## Internal Energies

The hydrogen and oxygen are gases. The product of the reaction is water vapor and it is also a gas at such an extreme temperature. Thermodynamics provides us with the formula for the internal energy of the gases:

$$U = c_v n R T \quad (3)$$

where:

- $U$  is internal energy
- $c_v$  is specific heat capacity at constant volume, approximately  $5/2$  for diatomic gas
- $n$  is amount of substance in moles
- $R$  is gas constant (0.08206)
- $T$  is absolute temperature.

Hydrogen and oxygen both are diatomic gases and the amount of substance equals to 3 moles according to (2).

The internal energy of initial reactants (hydrogen plus oxygen) will be equal according to (3) approximately to 184 Joules.

The temperature of product water vapor will be approximately equal to hydrogen adiabatic flame temperature of 3080K (when oxygen is oxidizer).

Specific molar heat capacity of water vapor according to Wikipedia ([https://en.wikipedia.org/wiki/Molar\\_heat\\_capacity](https://en.wikipedia.org/wiki/Molar_heat_capacity)) equals to 38.4 at 500°C and 59.7 at 5000°C. I am not going to search for heat capacity at 3000°C and will use the lower value of 38.4.

The internal energy of water vapor according to (3) will be 19400.

100 times fold could not be explained by calculation tolerances.

## **Conclusion**

The first law of thermodynamic (1) could not be hold along with the expression for internal energy (3) of an ideal gases at the same time. One of the expressions is not correct.

It is also possible that the usage of the first law should be limited to certain processes. Well, on second thought maybe not. How do you like - “Energy conservation does not hold for chemical reactions”?